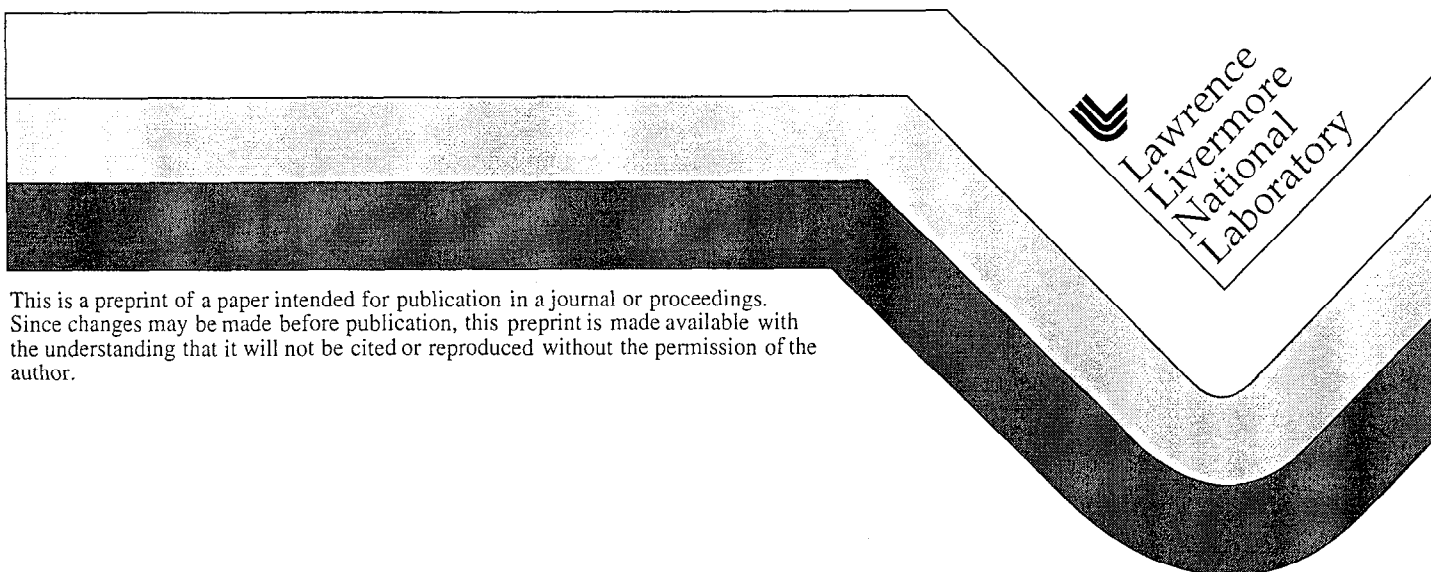


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ELECTRON FIELD EMISSION FROM UNDOPED AND DOPED DLC FILMS

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ABSTRACT

Electron field emission and electrical conductivity of undoped and nitrogen doped DLC films have been investigated. The films were grown by the PE CVD method from $\text{CH}_4:\text{H}_2$ and $\text{CH}_4:\text{H}_2:\text{N}_2$ gas mixtures, respectively. By varying nitrogen content in the gas mixture over the range 0 to 45%, corresponding concentrations of 0 to 8 % (atomic) could be achieved in the films. Three different gas pressures were used in the deposition chamber: 0.2, 0.6 and 0.8 Torr. Emission current measurements were performed at approximately 10^{-6} Torr using the diode method with emitter-anode spacing set at 20 μm . The current - voltage characteristics of the Si field electron emission arrays covered with DLC films show that threshold voltage (V_{th}) varies in a complex manner with nitrogen content. As a function of nitrogen content, V_{th} initially increases rapidly, then decreases and finally increases again for the highest concentration. Corresponding Fowler-Nordheim (F-N) plots follow F-N tunneling over a wide range. The F-N plots were used for determination of the work function, threshold voltage, field enhancement factor and effective emission area. For a qualitative explanation of experimental results, we treat the DLC film as a diamond-like (sp^3 bonded) matrix with graphite-like inclusions.

INTRODUCTION

DLC films are very attractive for field emitter applications. Previous results demonstrated improved field emission from silicon tips by coating DLC films [1-6]. Also, nitrogen doping is known to strongly influence emission properties of DLC films [7-10]. Nevertheless, the effect of deposition conditions and nitrogen doping on field emission properties of DLC films remains poorly understood.

In this work, the electron field emission properties of silicon tip arrays coated with undoped and nitrogen doped DLC films are investigated. The properties of the DLC films strongly depend on the microstructure which can be varied by the deposition conditions. The influence of DLC deposition conditions on electron field emission is studied in detail. The correlation between the film properties and field emission characteristics is investigated.

EXPERIMENT

Cathode formation

The arrays of silicon emitter tips were fabricated by wet chemical etching of (100) Si n-type wafers ($N_d=10^{15} \text{ cm}^{-3}$) patterned with Si_3N_4 masking material. Tip sharpening was performed by oxidation of the as-etched tips at 900°C in wet oxygen. The oxide formed is then removed in $\text{HF}:\text{H}_2\text{O}$ solution. This sharpening technique allows the production of tips with a radius of curvature of 10-20 nm and height of 4 μm . Our arrays have been fabricated over areas of 8x8 cm^2 with 2.5×10^5 tips/ cm^2 . The radii before and after DLC film deposition were estimated by scanning electron microscopy.

DLC films with thickness in the range 60-80nm were grown on flat silicon wafers and silicon tip arrays by plasma enhanced chemical vapor deposition (PE CVD) from a $\text{CH}_4:\text{H}_2:\text{N}_2$ mixture. Nitrogen content in the gas mixture was varied within the range from 0 to 45%. In-situ-gas-phase doping allowed DLC films to be deposited with controlled nitrogen content. Increasing the N_2 flow increases the N_2 content in the DLC films (Fig.1). DLC films were deposited under three levels of

gas pressure in the chamber: 0.2, 0.6 and 0.8 Torr. The substrates for deposition of DLC films were put directly on the 200 mm diameter cathode which was cooled by water and capacitively connected to a 13.36 MHz generator. During the plasma deposition experiments, the RF bias was ~1900 Volts. The DLC coatings were smooth and have reproducible properties from sample to sample under the same deposition conditions. The quality of the DLC coating on the tips was verified in the SEM.

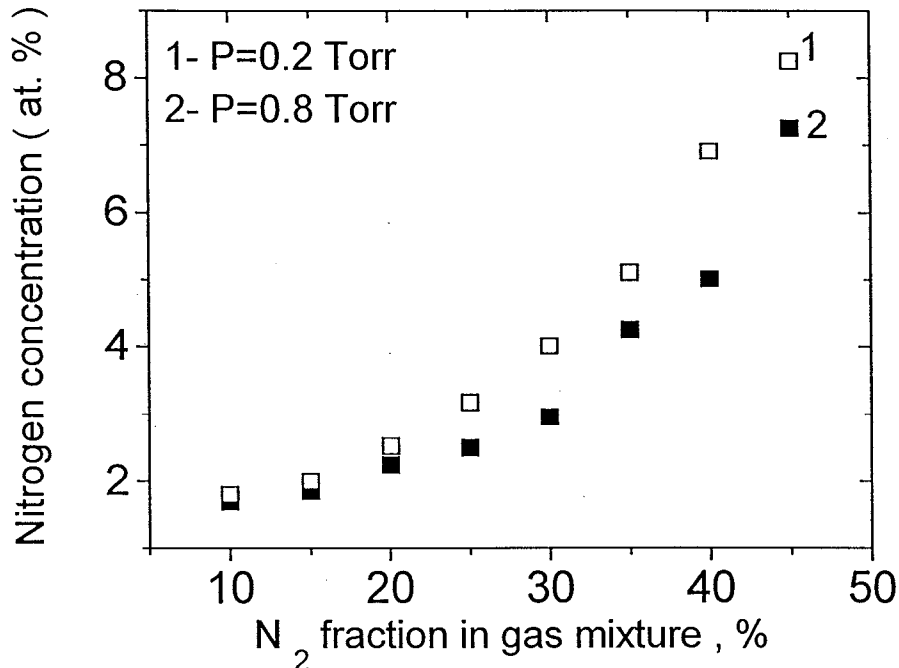


Fig.1. Nitrogen concentration in DLC film vs. nitrogen fraction in the gas mixture: 1-P=0.2 Torr; 2-P=0.8 Torr.

Measurements

Emission current was measured using a simple diode structure in a vacuum system pumped to a stable pressure of 10^{-6} Torr. A silicon wafer was used as the cathode and a molybdenum wire or quartz plate coated with ITO (indium-tin oxide) was used as the anode. A 20 micron thick teflon film spacer separated the anode and cathode plates. A 0.56 M Ω resistor was placed in series with the cathode to provide short-circuit protection and the emission current-voltage characteristics were obtained with a current sensitivity of 5 nA over a voltage range up to 1500 V.

After the tip array ($8 \times 8 \text{ cm}^2$) was completely fabricated, 1 cm^2 squares were cut from the wafer and mounted into the vacuum station. The control silicon emitter tip array (without coating) was dipped in a 5% HF solution for 20 s to remove the native oxide layer immediately before mounting in the HV system. The area investigated for each cathode measurement was $5.5 \times 10^{-3} \text{ cm}^2$ and contained 1.4×10^3 tips.

The resistivity of the DLC films was determined from I-V curves of MIS (metal-insulator-silicon) structures at an electric field strength of 10^6 V/cm . The thickness and refractive index of the DLC films on flat silicon wafers was measured with laser ellipsometry ($\lambda=632.8 \text{ nm}$). To estimate the nitrogen content in the DLC films, Auger spectroscopy was used.

RESULTS AND DISCUSSION

The flow of N₂ in the SiH₄:H₂:N₂ gas mixture was varied to control the N content in the DLC films grown onto the Si tips. The current - voltage characteristics of the Si field emission arrays covered with undoped and nitrogen doped DLC films are presented in Fig. 2a. At the beginning, the

threshold voltage (V_{th}) increases markedly with nitrogen content, then a reduction in V_{th} is observed and finally V_{th} increases again. Corresponding Fowler-Nordheim (F-N) plots are shown in Fig. 2b. The curves follow F-N tunneling over a wide range in electrical field.

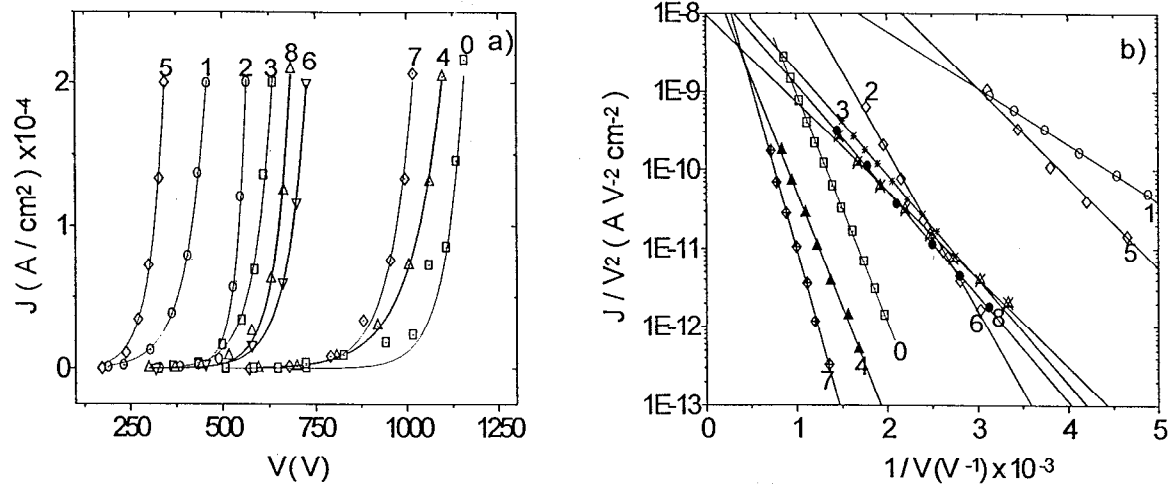


Fig.2. Current - voltage characteristics and corresponding Fowler-Nordheim plots of the Si tip arrays coated with undoped and gas phase doped DLC films: 0-Si tip array; (1-8) Si tip arrays +DLC: 1 - C(N₂) - 0% 2 - 5%; 3 - 10%; 4 - 15%; 5 - 20%; 6 - 25%; 7 - 30%; 8 - 35% (P=0.8 Torr, C(N₂) - nitrogen content in gas mixture under PE CVD deposition).

The F-N plots were used for determination of the threshold (turn-on) voltage, work function, field enhancement coefficients and effective emission areas according to the procedure described in Refs.11-13. It is impossible to independently determine two parameters: the field enhancement coefficient (β) and work function (Φ) from the Fowler-Nordheim plot alone. The field enhancement coefficients were calculated from the geometry of the emitting system according to

$$\beta E = hV / ((r+d)L) \quad (1)$$

where h is the height of the tip, V is the applied voltage, r is the radius of the tip estimated with SEM, d is the thickness of DLC film and L is the emitter-anode spacing. For the case of silicon tips without DLC coatings, β was determined from the Fowler-Nordheim plot for silicon ($\Phi=4.15$ eV). Good agreement is observed for Φ calculated from equation (1) for the case $d=0$ and determined from the Fowler-Nordheim plot.

The effective work function for different DLC film coatings was determined from the slope of the Fowler-Nordheim plots (b) using the calculated β coefficient. The relationship of the work functions of two materials (silicon and silicon covered with DLC films) was used,

$$\Phi_1 / \Phi_2 = (b_1 \beta_1 / b_2 \beta_2)^{2/3} \quad (2)$$

where Φ_i , β_i and b_i are the work functions, field enhancement coefficients and curve slopes in the Fowler-Nordheim equation, respectively, and index $i=1$ for uncoated and $i=2$ for DLC coated silicon tips.

The dependences of threshold voltage and effective work function of the Si tip array and arrays coated with DLC films on the N₂ content in the gas mixture are summarized in Table 1 and Figs. 3,4. Non-monotonic dependence on N content is found.

The effective work function generally increases from 0 to 15% and decreases from 15 to 25%. At still higher N₂ concentration, Φ increases again. The lowest value of $\Phi=0.92$ eV was obtained for DLC films deposited for N₂=25% in the gas mixture and P=0.6 Torr. A significant influence of the gas pressure on effective work function is also observed, the lowest being achieved at the intermediate pressure, P=0.6 Torr. As can be seen from Figs.3 and 4, some correlation exists in V_{th} and Φ dependencies, namely a minimum near 25%.

Table 1. Characteristic parameters of tip arrays with DLC coating (P=0.6 Torr).

d, nm	N ₂ %	N, at. %	$\beta/L, \text{cm}^{-1}$	V _{th} , V	Φ , eV
0	-	0	1.15×10^5	507	4.15
58	0	0	2.66×10^4	196	0.99
60	5	1.5	2.58×10^4	273	0.99
64	15	1.7	2.46×10^4	294	1.4
71	20	2.06	2.26×10^4	209	1.0
74	25	2.58	2.19×10^4	121	0.92
76	30	3.67	2.14×10^4	238	0.98
81	35	4.4	2.03×10^4	322	1.58
70	40	5.12	2.29×10^4	714	2.31
82	45	7.5	2.01×10^4	507	2.83

The optical band gap of DLC films has been measured by using spectroscopic ellipsometry. The band gap is changed significantly with N content with the smallest value $E_g=2\text{eV}$, observed for the 15% gas mixture (Fig.5) which corresponds to 1.7% atomic nitrogen incorporated in the film (see Table 1). Values of the band gap rise to 4eV at the highest nitrogen content. Our results concerning the influence of the nitrogen doping on DLC film properties are generally in agreement with data obtained by other authors [7,8,11].

Nitrogen atoms in DLC films change the band gap (see Fig.5) and stabilize carbon atoms in sp^3 hybridization with the creation of C-N bonds. According to model of the DLC films as a diamond-like matrix with graphite-like inclusions in it, these films are not a homogeneous material and have the thickness and spatial heterogeneity caused by the deposition conditions. To characterize such films we use an "effective" work function.

The non-monotonic dependencies of E_g (Fig. 5) on nitrogen content in the gas mixture may be interpreted in the framework of the model taking into account the effect of nitrogen on the film

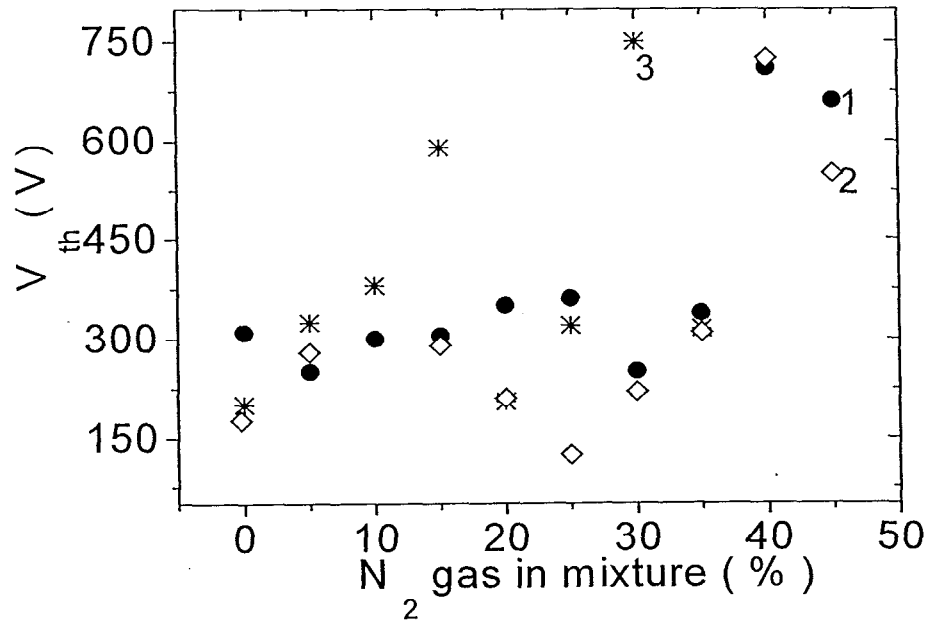


Fig 3. Threshold voltage dependencies for electron field emission from silicon tips+DLC films versus nitrogen content in the gas mixture (1 - P=0.2 Torr, 2 - P= 0.6 Torr, 3 - P=0.8 Torr).

structure. At low concentration, the nitrogen atoms fit into the film at sp^2 -cluster boundaries increasing the fraction of the disordered sp^2 -phase [12,13]. This, in turn, must result in E_g decreasing, as observed (see Fig 5). On further increasing the nitrogen content in the film, the excess nitrogen atoms begin to fit in between the sp^2 -clusters. This causes strain relaxation in the film and stimulates formation of sp^3 -coordinated carbon-hydrogen bonds. As this takes place, E_g increases.

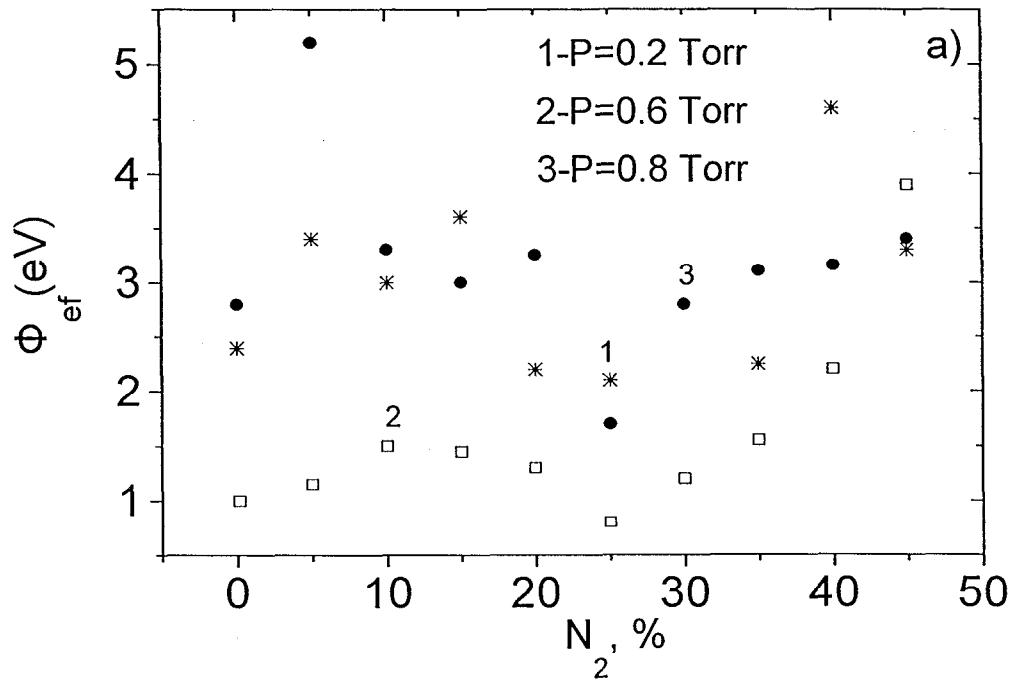


Fig 4. Effective work function for electron field emission from silicon tips+DLC films, versus nitrogen content in the gas mixture (1 - P=0.2 Torr, 2 - P= 0.6 Torr, 3 - P=0.8 Torr)

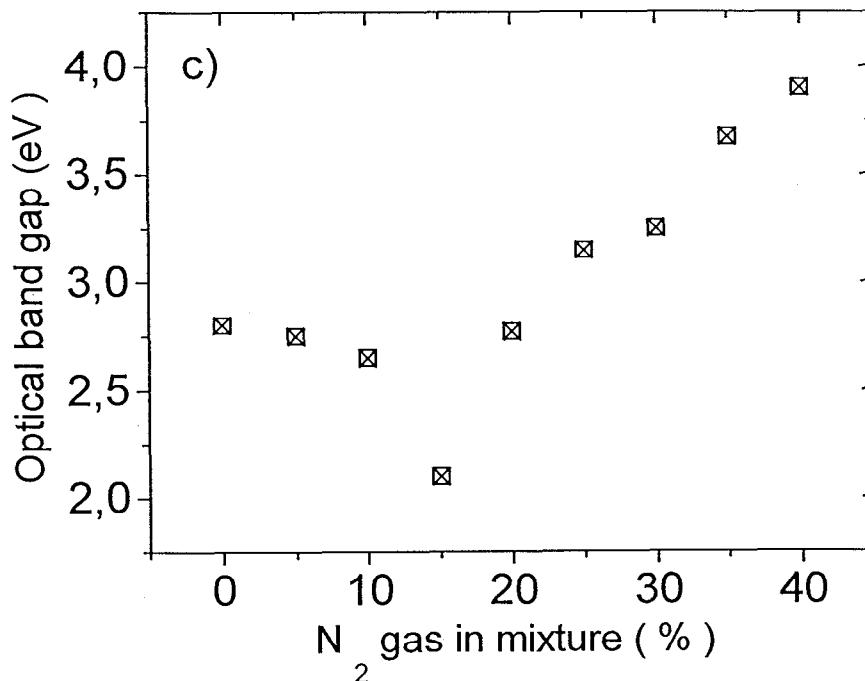


Fig.5. Dependence of optical band gap for DLC films on the N content in gas mixtures (p=0.8 Torr)

The relationship among work function, electron emission and conductivity should be studied further to clarify the emission mechanism of DLC films.

CONCLUSION

We have studied electron field emission from silicon tip arrays coated with undoped and nitrogen doped DLC films. The doping level was changed by varying the nitrogen content in the gas mixture $\text{CH}_4:\text{H}_2:\text{N}_2$. Complex dependencies of effective work function, threshold voltage, resistivity and optical band gap on nitrogen content in the DLC film are observed. The minimum effective work function, 0.92 eV, was obtained at $\text{N}_2=25\%$ in the gas mixture, corresponding to 2.58% atomic in the film grown. Using a silicon tip array covered with undoped and in-situ nitrogen doped DLC films leads to a remarkable increase in electron emission current in comparison with uncoated arrays.

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